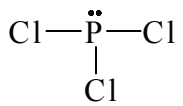
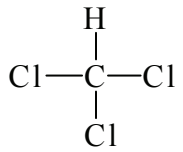
CHAPTER 10
CHEMICAL BONDING II: MOLECULAR GEOMETRY AND HYBRIDIZATION OF ATOMIC ORBITALS

10.7 **(a)** The Lewis structure of PCl_3 is shown below. Since in the VSEPR method the number of bonding pairs and lone pairs of electrons around the *central atom* (phosphorus, in this case) is important in determining the structure, the lone pairs of electrons around the chlorine atoms have been omitted for simplicity. There are three bonds and one lone electron pair around the central atom, phosphorus, which makes this an AB_3E case. The information in Table 10.2 shows that the structure is a trigonal pyramid like ammonia.

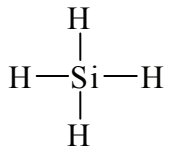


What would be the structure of the molecule if there were no lone pairs and only three bonds?

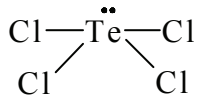
(b) The Lewis structure of $CHCl_3$ is shown below. There are four bonds and no lone pairs around carbon which makes this an AB_4 case. The molecule should be tetrahedral like methane (Table 10.1).



(c) The Lewis structure of SiH_4 is shown below. Like part (b), it is a tetrahedral AB_4 molecule.



(d) The Lewis structure of $TeCl_4$ is shown below. There are four bonds and one lone pair which make this an AB_4E case. Consulting Table 10.2 shows that the structure should be that of a distorted tetrahedron like SF_4.

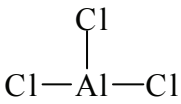
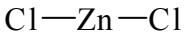
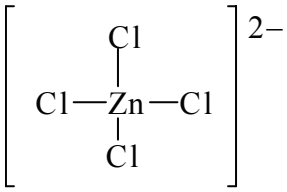


Are $TeCl_4$ and SF_4 isoelectronic? Should isoelectronic molecules have similar VSEPR structures?

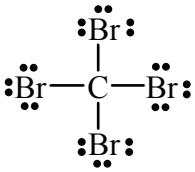
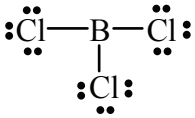
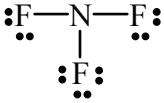
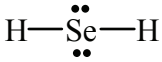
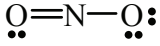
10.8 **Strategy:** The sequence of steps in determining molecular geometry is as follows:

draw Lewis structure ⟶ find arrangement of electrons pairs ⟶ find arrangement of bonding pairs ⟶ determine geometry based on bonding pairs

Solution:

Lewis structure	Electron pairs on central atom	Electron arrangement	Lone pairs	Geometry
(a) 	3	trigonal planar	0	trigonal planar, AB_3
(b) 	2	linear	0	linear, AB_2
(c) 	4	tetrahedral	0	tetrahedral, AB_4

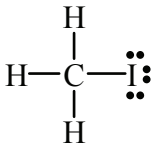
10.9

	Lewis Structure	e^- pair arrangement	geometry
(a)		tetrahedral	tetrahedral
(b)		trigonal planar	trigonal planar
(c)		tetrahedral	trigonal pyramidal
(d)		tetrahedral	bent
(e)		trigonal planar	bent

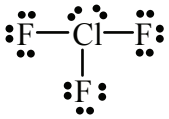
10.10 We use the following sequence of steps to determine the geometry of the molecules.

draw Lewis structure ⟶ find arrangement of electrons pairs ⟶ find arrangement of bonding pairs ⟶ determine geometry based on bonding pairs

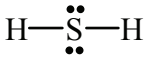
(a) Looking at the Lewis structure we find 4 pairs of electrons around the central atom. The electron pair arrangement is tetrahedral. Since there are no lone pairs on the central atom, the geometry is also **tetrahedral**.



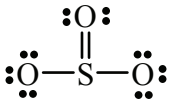
(b) Looking at the Lewis structure we find 5 pairs of electrons around the central atom. The electron pair arrangement is trigonal bipyramidal. There are two lone pairs on the central atom, which occupy positions in the trigonal plane. The geometry is **t-shaped**.



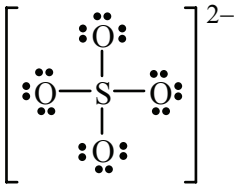
(c) Looking at the Lewis structure we find 4 pairs of electrons around the central atom. The electron pair arrangement is tetrahedral. There are two lone pairs on the central atom. The geometry is **bent**.



(d) Looking at the Lewis structure, there are 3 VSEPR pairs of electrons around the central atom. Recall that a double bond counts as one VSEPR pair. The electron pair arrangement is trigonal planar. Since there are no lone pairs on the central atom, the geometry is also **trigonal planar**.

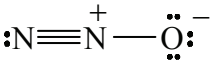


(e) Looking at the Lewis structure, there are 4 pairs of electrons around the central atom. The electron pair arrangement is tetrahedral. Since there are no lone pairs on the central atom, the geometry is also **tetrahedral**.

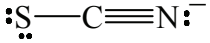


10.11 The lone pairs of electrons on the bromine atoms have been omitted for simplicity.

linear



linear

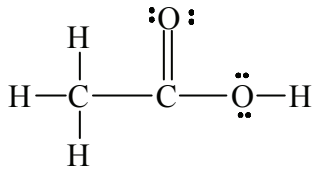


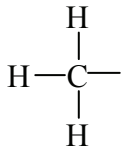
linear

10.12

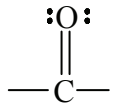
(a)	AB_4	tetrahedral	**(f)**	AB_4	tetrahedral
(b)	AB_2E_2	bent	**(g)**	AB_5	trigonal bipyramidal
(c)	AB_3	trigonal planar	**(h)**	AB_3E	trigonal pyramidal
(d)	AB_2E_3	linear	**(i)**	AB_4	tetrahedral
(e)	AB_4E_2	square planar			

10.13 The Lewis structure is:

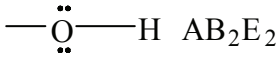




AB_4 tetrahedral

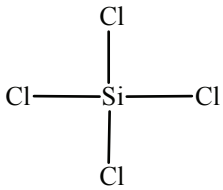


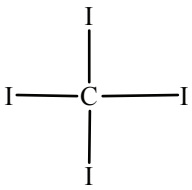
AB_3 trigonal planar

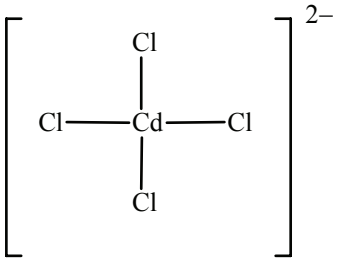


AB_2E_2 bent

10.14 Only molecules with four bonds to the central atom and no lone pairs are tetrahedral (AB_4).







What are the Lewis structures and shapes for XeF_4 and SeF_4?

10.19 All four molecules have two bonds and two lone pairs (AB_2E_2) and therefore the bond angles are not linear. Since electronegativity decreases going down a column (group) in the periodic table, the electronegativity differences between hydrogen and the other Group 6 element will increase in the order Te < Se < S < O. The dipole moments will increase in the same order. Would this conclusion be as easy if the elements were in different groups?

10.20 The electronegativity of the halogens decreases from F to I. Thus, the polarity of the H–X bond (where X denotes a halogen atom) also decreases from HF to HI. This difference in electronegativity accounts for the decrease in dipole moment.

10.21 $CO_2 = CBr_4$ ($\mu = 0$ for both) $< H_2S < NH_3 < H_2O < HF$

10.22 Draw the Lewis structures. Both molecules are linear (AB_2). In CS_2, the two C–S bond moments are equal in magnitude and opposite in direction. The sum or resultant dipole moment will be *zero*. Hence, CS_2 is a nonpolar molecule. Even though OCS is linear, the C–O and C–S bond moments are not exactly equal, and there will be a small net dipole moment. Hence, OCS has a **larger** dipole moment than CS_2 (zero).

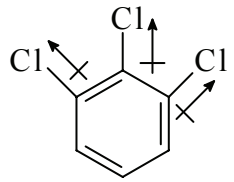
10.23 Molecule **(b)** will have a higher dipole moment. In molecule (a), the *trans* arrangement cancels the bond dipoles and the molecule is nonpolar.

10.24 **Strategy:** Keep in mind that the dipole moment of a molecule depends on both the difference in electronegativities of the elements present and its geometry. A molecule can have polar bonds (if the bonded atoms have different electronegativities), but it may not possess a dipole moment if it has a highly symmetrical geometry.

Solution: Each vertex of the hexagonal structure of benzene represents the location of a C atom. Around the ring, there is no difference in electronegativity between C atoms, so the only bonds we need to consider are the polar C–Cl bonds.

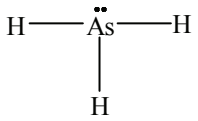
The molecules shown in **(b)** and **(d)** are nonpolar. Due to the high symmetry of the molecules and the equal magnitude of the bond moments, the bond moments in each molecule cancel one another. The resultant dipole moment will be *zero*. For the molecules shown in **(a)** and **(c),** the bond moments do not cancel and there will be net dipole moments. The dipole moment of the molecule in **(a)** is larger than that in **(c)**, because in **(a)** all the bond moments point in the same relative direction, reinforcing each other (see Lewis structure below). Therefore, the order of increasing dipole moments is:

(b) = (d) < (c) < (a).



(a)

10.33 AsH_3 has the Lewis structure shown below. There are three bond pairs and one lone pair. The four electron pairs have a tetrahedral arrangement, and the molecular geometry is trigonal pyramidal (AB_3E) like ammonia (See Table 10.2). The As (arsenic) atom is in an sp^3 hybridization state.



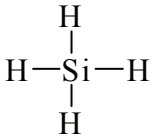
Three of the sp^3 hybrid orbitals form bonds to the hydrogen atoms by overlapping with the hydrogen 1*s* orbitals. The fourth sp^3 hybrid orbital holds the lone pair.

10.34 **Strategy:** The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule → use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text) → use Table 10.4 of the text to determine the hybridization state of the central atom

Solution:

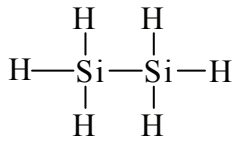
(a) Write the Lewis structure of the molecule.



Count the number of electron pairs around the central atom. Since there are four electron pairs around Si, the electron arrangement that minimizes electron-pair repulsion is **tetrahedral**.

We conclude that Si is ***sp*^{3} hybridized** because it has the electron arrangement of four sp^3 hybrid orbitals.

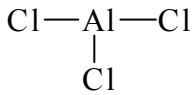
(b) Write the Lewis structure of the molecule.

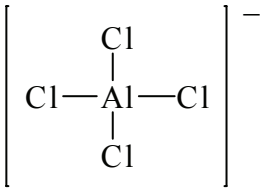


Count the number of electron pairs around the "central atoms". Since there are four electron pairs around each Si, the electron arrangement that minimizes electron-pair repulsion for each Si is **tetrahedral**.

We conclude that each Si is ***sp*^{3} hybridized** because it has the electron arrangement of four sp^3 hybrid orbitals.

10.35 The Lewis structures of $AlCl_3$ and $AlCl_4^-$ are shown below. By the reasoning of the two problems above, the hybridization changes from sp^2 to sp^3.





What are the geometries of these molecules?

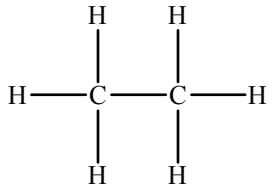
10.36 Draw the Lewis structures. Before the reaction, boron is sp^2 hybridized (trigonal planar electron arrangement) in BF_3 and nitrogen is sp^3 hybridized (tetrahedral electron arrangement) in NH_3. After the reaction, boron and nitrogen are both sp^3 hybridized (tetrahedral electron arrangement).

10.37 **(a)** NH_3 is an AB_3E type molecule just as AsH_3 in Problem 10.33. Referring to Table 10.4 of the text, the nitrogen is sp^3 hybridized.

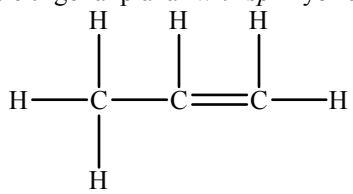
(b) N_2H_4 has two equivalent nitrogen atoms. Centering attention on just one nitrogen atom shows that it is an AB_3E molecule, so the nitrogen atoms are sp^3 hybridized. From structural considerations, how can N_2H_4 be considered to be a derivative of NH_3?

(c) The nitrate anion NO_3^- is isoelectronic and isostructural with the carbonate anion CO_3^{2-} that is discussed in Example 9.5 of the text. There are three resonance structures, and the ion is of type AB_3; thus, the nitrogen is sp^2 hybridized.

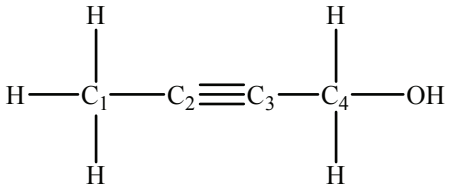
10.38 **(a)** Each carbon has four bond pairs and no lone pairs and therefore has a tetrahedral electron pair arrangement. This implies sp^3 hybrid orbitals.



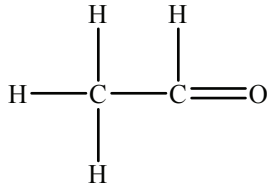
(b) The left-most carbon is tetrahedral and therefore has sp^3 hybrid orbitals. The two carbon atoms connected by the double bond are trigonal planar with sp^2 hybrid orbitals.



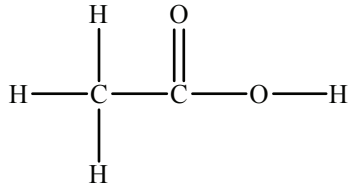
(c) Carbons 1 and 4 have sp^3 hybrid orbitals. Carbons 2 and 3 have *sp* hybrid orbitals.



(d) The left-most carbon is tetrahedral (sp^3 hybrid orbitals). The carbon connected to oxygen is trigonal planar (why?) and has sp^2 hybrid orbitals.



(e) The left-most carbon is tetrahedral (sp^3 hybrid orbitals). The other carbon is trigonal planar with sp^2 hybridized orbitals.



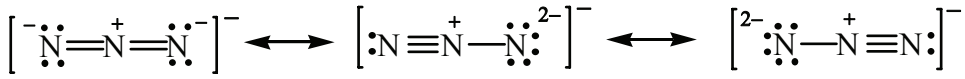
10.39 **(a)** *sp* **(b)** *sp* **(c)** *sp*

10.40 **Strategy:** The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule → use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text) → use Table 10.4 of the text to determine the hybridization state of the central atom

Solution:

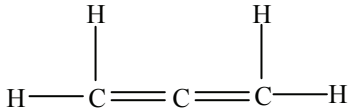
Write the Lewis structure of the molecule. Several resonance forms with formal charges are shown.



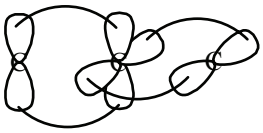
Count the number of electron pairs around the central atom. Since there are two electron pairs around N, the electron arrangement that minimizes electron-pair repulsion is **linear** (AB_2). Remember, for VSEPR purposes a multiple bond counts the same as a single bond.

We conclude that N is ***sp* hybridized** because it has the electron arrangement of two *sp* hybrid orbitals.

10.41 The Lewis structure is shown below. The two end carbons are trigonal planar and therefore use sp^2 hybrid orbitals. The central carbon is linear and must use *sp* hybrid orbitals.



A Lewis drawing does not necessarily show actual molecular geometry. Notice that the two CH_2 groups at the ends of the molecule must be perpendicular. This is because the two double bonds must use different 2*p* orbitals on the middle carbon, and these two 2*p* orbitals are perpendicular. The overlap of the 2*p* orbitals on each carbon is shown below.



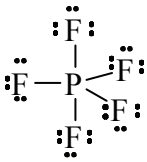
Is the allene molecule polar?

10.42 **Strategy:** The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule → use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text) → use Table 10.4 of the text to determine the hybridization state of the central atom

Solution:

Write the Lewis structure of the molecule.



Count the number of electron pairs around the central atom. Since there are five electron pairs around P, the electron arrangement that minimizes electron-pair repulsion is **trigonal bipyramidal** (AB_5).

We conclude that P is ***sp*^{3}*d* hybridized** because it has the electron arrangement of five sp^3d hybrid orbitals.

10.43 It is almost always true that a single bond is a sigma bond, that a double bond is a sigma bond and a pi bond, and that a triple bond is *always* a sigma bond and two pi bonds.

(a) sigma bonds: 4; pi bonds: 0 **(b)** sigma bonds: 5; pi bonds: 1
(c) sigma bonds: 10; pi bonds: 3

10.44 A single bond is usually a sigma bond, a double bond is usually a sigma bond and a pi bond, and a triple bond is always a sigma bond and two pi bonds. Therefore, there are **nine pi bonds** and **nine sigma bonds** in the molecule.

10.49 The molecular orbital electron configuration and bond order of each species is shown below.

	H_2	H_2^+	H_2^{2+}
$\sigma_{1s}^\star$	___	___	
σ_{1s}	↑↓	↑	

bond order = 1 bond order = $\frac{1}{2}$ bond order = 0

The internuclear distance in the +1 ion should be greater than that in the neutral hydrogen molecule. The distance in the +2 ion will be arbitrarly large because there is no bond (bond order zero).

10.50 In order for the two hydrogen atoms to combine to form a H_2 molecule, the electrons must have opposite spins. Furthermore, the combined energy of the two atoms must not be too great. Otherwise, the H_2 molecule will possess too much energy and will break apart into two hydrogen atoms.

10.51 The energy level diagrams are shown below.

	He_2	HHe	He_2^+
$\sigma_{1s}^\star$	↑↓	↑	↑
σ_{1s}	↑↓	↑↓	↑↓

bond order = 0 bond order = $\frac{1}{2}$ bond order = $\frac{1}{2}$

He_2 has a bond order of zero; the other two have bond orders of 1/2. Based on bond orders alone, He_2 has no stability, while the other two have roughly equal stabilities.

10.52 The electron configurations are listed. Refer to Table 10.5 of the text for the molecular orbital diagram.

Li_2: $(\sigma_{1s})^2(\sigma_{1s}^\star)^2(\sigma_{2s})^2$ bond order = 1

Li_2^+: $(\sigma_{1s})^2(\sigma_{1s}^\star)^2(\sigma_{2s})^1$ bond order = $\frac{1}{2}$

Li_2^-: $(\sigma_{1s})^2(\sigma_{1s}^\star)^2(\sigma_{2s})^2(\sigma_{2s}^\star)^1$ bond order = $\frac{1}{2}$

Order of increasing stability: $\mathbf{Li_2^-} = \mathbf{Li_2^+} < \mathbf{Li_2}$

In reality, Li_2^+ is more stable than Li_2^- because there is less electrostatic repulsion in Li_2^+.

10.53 The Be_2 molecule does not exist because there are equal numbers of electrons in bonding and antibonding molecular orbitals, making the bond order zero.

$\sigma^{\star}_{2s}$	↑↓
σ_{2s}	↑↓
$\sigma^{\star}_{1s}$	↑↓
σ_{1s}	↑↓

bond order = 0

10.54 See Table 10.5 of the text. Removing an electron from B_2 (bond order = 1) gives B_2^+, which has a bond order of (1/2). Therefore, $\mathbf{B_2^+}$ has a weaker and longer bond than B_2.

10.55 The energy level diagrams are shown below.

	C_2^{2-}			C_2		
$\sigma^{\star}_{2p_x}$				$\sigma^{\star}_{2p_x}$		
$\pi^{\star}_{2p_y}$, $\pi^{\star}_{2p_z}$				$\pi^{\star}_{2p_y}$, $\pi^{\star}_{2p_z}$		
σ_{2p_x}	↑↓			σ_{2p_x}		
π_{2p_y}, π_{2p_z}	↑↓	↑↓		π_{2p_y}, π_{2p_z}	↑↓	↑↓
$\sigma^{\star}_{2s}$	↑↓			$\sigma^{\star}_{2s}$	↑↓	
σ_{2s}	↑↓			σ_{2s}	↑↓	
$\sigma^{\star}_{1s}$	↑↓			$\sigma^{\star}_{1s}$	↑↓	
σ_{1s}	↑↓			σ_{1s}	↑↓	

The bond order of the carbide ion is 3 and that of C_2 is only 2. With what homonuclear diatomic molecule is the carbide ion isoelectronic?

10.56 In both the Lewis structure and the molecular orbital energy level diagram (Table 10.5 of the text), the oxygen molecule has a double bond (bond order = 2). The principal difference is that the molecular orbital treatment predicts that the molecule will have two unpaired electrons (paramagnetic). Experimentally this is found to be true.

10.57 In forming the N_2^+ from N_2, an electron is removed from the sigma *bonding* molecular orbital. Consequently, the bond order decreases to 2.5 from 3.0. In forming the O_2^+ ion from O_2, an electron is removed from the pi *antibonding* molecular orbital. Consequently, the bond order increases to 2.5 from 2.0.

10.58 We refer to Table 10.5 of the text.

O_2 has a bond order of 2 and is paramagnetic (two unpaired electrons).

O_2^+ has a bond order of 2.5 and is paramagnetic (one unpaired electron).

O_2^- has a bond order of 1.5 and is paramagnetic (one unpaired electron).

O_2^{2-} has a bond order of 1 and is diamagnetic.

Based on molecular orbital theory, the stability of these molecules increases as follows:

$$\mathbf{O_2^{2-} < O_2^{-} < O_2 < O_2^{+}}$$

10.59 From Table 10.5 of the text, we see that the bond order of F_2^+ is 1.5 compared to 1 for F_2. Therefore, F_2^+ should be more stable than F_2 (stronger bond) and should also have a shorter bond length.

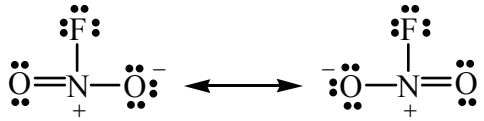
10.60 As discussed in the text (see Table 10.5), the single bond in B_2 is a pi bond (the electrons are in a pi *bonding* molecular orbital) and the double bond in C_2 is made up of two pi bonds (the electrons are in the pi *bonding* molecular orbitals).

10.63 Benzene is stabilized by delocalized molecular orbitals. The C–C bonds are equivalent, rather than alternating single and double bonds. The additional stabilization makes the bonds in benzene much less reactive chemically than isolated double bonds such as those in ethylene.

10.64 The symbol on the left shows the pi bond delocalized over the entire molecule. The symbol on the right shows only one of the two resonance structures of benzene; it is an incomplete representation.

10.65 If the two rings happen to be perpendicular in biphenyl, the pi molecular orbitals are less delocalized. In naphthalene the pi molecular orbital is always delocalized over the entire molecule. What do you think is the most stable structure for biphenyl: both rings in the same plane or both rings perpendicular?

10.66 **(a)** Two Lewis resonance forms are shown below. Formal charges different than zero are indicated.



(b) There are no lone pairs on the nitrogen atom; it should have a trigonal planar electron pair arrangement and therefore use $\boldsymbol{sp^2}$ hybrid orbitals.

(c) The bonding consists of sigma bonds joining the nitrogen atom to the fluorine and oxygen atoms. In addition there is a pi molecular orbital delocalized over the N and O atoms. Is nitryl fluoride isoelectronic with the carbonate ion?

10.67 The ion contains 24 valence electrons. Of these, six are involved in three sigma bonds between the nitrogen and oxygen atoms. The hybridization of the nitrogen atom is sp^2. There are 16 non-bonding electrons on the oxygen atoms. The remaining two electrons are in a delocalized pi molecular orbital which results from the overlap of the p_z orbital of nitrogen and the p_z orbitals of the three oxygen atoms. The molecular orbitals are similar to those of the carbonate ion (See Section 10.8 of the text).

10.68 The Lewis structures of ozone are:

The central oxygen atom is $\boldsymbol{sp^2}$ hybridized (AB_2E). The unhybridized $2p_z$ orbital on the central oxygen overlaps with the $2p_z$ orbitals on the two end atoms.

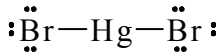
10.69 Only **(c)** will not be tetrahedral. All the others have AB_4–type Lewis structures and will therefore be tetrahedral. For SF_4 the Lewis structure is of the AB_4E type which gives rise to a distorted tetrahedral geometry (Table 10.2 of the text).

10.70 **Strategy:** The sequence of steps in determining molecular geometry is as follows:

draw Lewis structure ⟶ find arrangement of electrons pairs ⟶ find arrangement of bonding pairs ⟶ determine geometry based on bonding pairs

Solution:

Write the Lewis structure of the molecule.



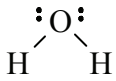
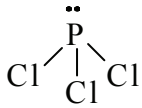
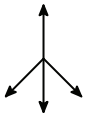
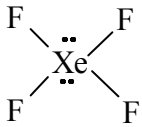
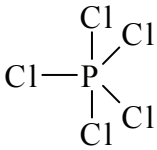
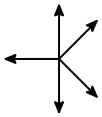
Count the number of electron pairs around the central atom. There are two electron pairs around Hg.

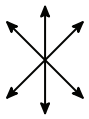
Since there are two electron pairs around Hg, the electron-pair arrangement that minimizes electron-pair repulsion is **linear**.

In addition, since there are no lone pairs around the central atom, the geometry is also **linear** (AB_2).

You could establish the geometry of $HgBr_2$ by measuring its dipole moment. If mercury(II) bromide were bent, it would have a measurable dipole moment. Experimentally, it has no dipole moment and therefore must be linear.

10.71

Dot structure	*Label*	*Shape*	*Bond dipole*	*Resultant*	*dipole moment*
	AB_2E_2	bent			$\mu > 0$
	AB_3E	trigonal pyramidal			$\mu > 0$
	AB_4E_2	square planar			$\mu = 0$
	AB_5	trigonal bipyramid			$\mu = 0$

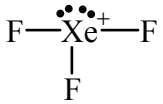
AB_6 octahedral  $\mu = 0$

Why do the bond dipoles add to zero in PCl_5?

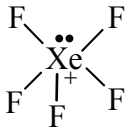
10.72 According to valence bond theory, a pi bond is formed through the side-to-side overlap of a pair of *p* orbitals. As atomic size increases, the distance between atoms is too large for *p* orbitals to overlap effectively in a side-to-side fashion. If two orbitals overlap poorly, that is, they share very little space in common, then the resulting bond will be very weak. This situation applies in the case of pi bonds between silicon atoms as well as between any other elements not found in the second period. It is usually far more energetically favorable for silicon, or any other heavy element, to form two single (sigma) bonds to two other atoms than to form a double bond (sigma + pi) to only one other atom.

10.73 Geometry: bent; hybridization: sp^3.

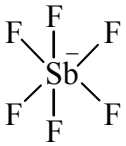
10.74 The Lewis structures and VSEPR geometries of these species are shown below. The three nonbonding pairs of electrons on each fluorine atom have been omitted for simplicity.



AB_3E_2
T-shaped

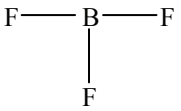


AB_5E
Square Pyramidal



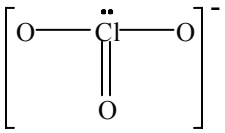
AB_6
Octahedral

10.75 **(a)** The Lewis structure is:



The shape will be trigonal ***planar*** (AB_3)

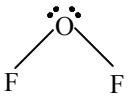
(b) The Lewis structure is:



The molecule will be a trigonal pyramid (***nonplanar***).

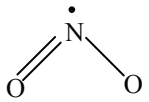
(c) The Lewis structure and the dipole moment for H_2O is presented in Problem 10.71. The dipole moment is directed from the positive hydrogen end to the more negative oxygen.

(d) The Lewis structure is:



The molecule is bent and therefore ***polar***.

(e) The Lewis structure is:



The nitrogen atom is of the AB_2E type, but there is only one unshared electron rather than the usual pair. As a result, the repulsion will not be as great and the O–N–O angle will be ***greater than 120°*** expected for AB_2E geometry. Experiment shows the angle to be around 135°.

Which of the species in this problem has resonance structures?

10.76 To predict the bond angles for the molecules, you would have to draw the Lewis structure and determine the geometry using the VSEPR model. From the geometry, you can predict the bond angles.

(a) $BeCl_2$: AB_2 type, 180° (linear).

(b) BCl_3: AB_3 type, 120° (trigonal planar).

(c) CCl_4: AB_4 type, 109.5° (tetrahedral).

(d) CH_3Cl: AB_4 type, 109.5° (tetrahedral with a possible slight distortion resulting from the different sizes of the chlorine and hydrogen atoms).

(e) Hg_2Cl_2: Each mercury atom is of the AB_2 type. The entire molecule is linear, 180° bond angles.

(f) $SnCl_2$: AB_2E type, roughly 120° (bent).

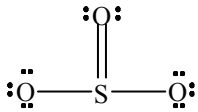
(g) H_2O_2: The atom arrangement is HOOH. Each oxygen atom is of the AB_2E_2 type and the H–O–O angles will be roughly 109.5°.

(h) SnH_4: AB_4 type, 109.5° (tetrahedral).

10.77 The two approaches are discussed in Sections 10.1, 10.3, and 10.4 of the textbook.

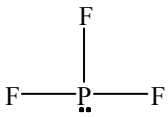
10.78 Since arsenic and phosphorus are both in the same group of the periodic table, this problem is exactly like Problem 10.42. AsF_5 is an AB_5 type molecule, so the geometry is trigonal bipyramidal. We conclude that As is ***sp^3d* hybridized** because it has the electron arrangement of five sp^3d hybrid orbitals.

10.79 **(a)** The Lewis structure is:



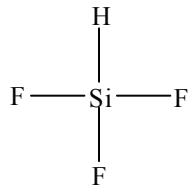
The geometry is trigonal planar; the molecule is ***nonpolar***.

(b) The Lewis structure is:



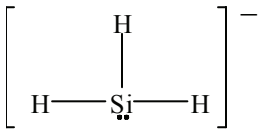
The molecule has trigonal pyramidal geometry. It is ***polar***.

(c) The Lewis structure is:



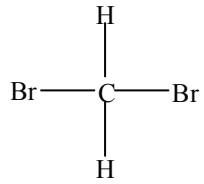
The molecule will be tetrahedral (AB_4). Both fluorine and hydrogen are more electronegative than silicon, but fluorine is the most electronegative element, so the molecule will be polar (fluorine side negative).

(d) The Lewis structure is:



The ion has a ***trigonal pyramidal*** geometry (AB_3E).

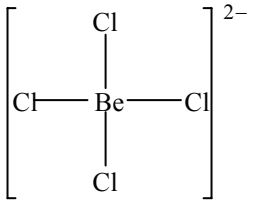
(e) The Lewis structure is:



The molecule will be tetrahedral (AB_4) but still ***polar***. The negative end of the dipole moment will be on the side with the two bromine atoms; the positive end will be on the hydrogen side.

10.80 Only ICl_2^- and $CdBr_2$ will be linear. The rest are bent.

10.81 The Lewis structure is shown below.



The molecule is of the AB_4 type and should therefore be ***tetrahedral***. The hybridization of the Be atom should be sp^3.

10.82 **(a)**

Strategy: The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule → use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text) → use Table 10.4 of the text to determine the hybridization state of the central atom

Solution:

The geometry around each nitrogen is identical. To complete an octet of electrons around N, you must add a lone pair of electrons. Count the number of electron pairs around N. There are three electron pairs around each N.

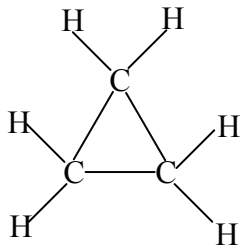
Since there are three electron pairs around N, the electron-pair arrangement that minimizes electron-pair repulsion is **trigonal planar**.

We conclude that each N is ***sp*^{2} hybridized** because it has the electron arrangement of three sp^2 hybrid orbitals.

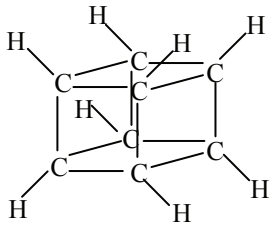
(b)
Strategy: Keep in mind that the dipole moment of a molecule depends on both the difference in electronegativities of the elements present and its geometry. A molecule can have polar bonds (if the bonded atoms have different electronegativities), but it may not possess a dipole moment if it has a highly symmetrical geometry.

Solution: An N–F bond is polar because F is more electronegative than N. The structure on the right has a dipole moment because the two N–F bond moments do not cancel each other out and so the molecule has a net dipole moment. On the other hand, the two N–F bond moments in the left-hand structure cancel. The sum or resultant dipole moment will be *zero*.

10.83 **(a)** The structures for cyclopropane and cubane are



Cyclopropane



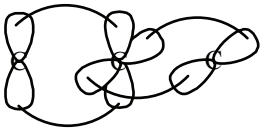
Cubane

(b) The C–C–C bond in cyclopropane is 60° and in cubane is 90°. Both are smaller than the 109.5° expected for sp^3 hybridized carbon. Consequently, there is considerable strain on the molecules.

(c) They would be more difficult to make than an sp^3 hybridized carbon in an unconstrained (that is, not in a small ring) system in which the carbons can adopt bond angles closer to 109.5°.

10.84 In 1,2-dichloroethane, the two C atoms are joined by a sigma bond. Rotation about a sigma bond does not destroy the bond, and the bond is therefore free (or relatively free) to rotate. Thus, all angles are permitted and the molecule is nonpolar because the C–Cl bond moments cancel each other because of the averaging effect brought about by rotation. In *cis*-dichloroethylene the two C–Cl bonds are locked in position. The π bond between the C atoms prevents rotation (in order to rotate, the π bond must be broken, using an energy source such as light or heat). Therefore, there is no rotation about the C=C in *cis*-dichloroethylene, and the molecule is polar.

10.85 Consider the overlap of the 2*p* orbitals on each carbon atom.

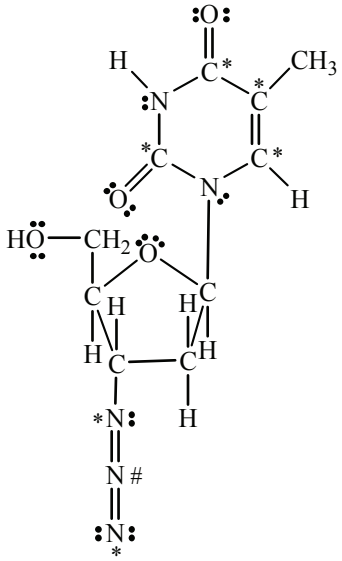


The geometric planes containing the CHCl groups at each end of the molecule are mutually perpendicular. This is because the two carbon-carbon double bonds must use different 2*p* orbitals on the middle carbon, and these two 2*p* orbitals are perpendicular. This means that the two chlorine atoms can be considered to be on one side of the molecule and the two hydrogen atoms on the other. The molecule has a dipole moment. Draw the end-on view if you aren't convinced.

10.86 O_3, CO, CO_2, NO_2, N_2O, CH_4, and $CFCl_3$ are greenhouse gases.

10.87 Both sulfur–to–oxygen bonds are double bonds which occupy more space than single bonds and the repulsion between the double bonds spread out the angle close to 120°.

10.88 The Lewis structure is:



The carbon atoms and nitrogen atoms marked with an asterisk (C∗ and N∗) are sp^2 hybridized; unmarked carbon atoms and nitrogen atoms are sp^3 hybridized; and the nitrogen atom marked with (#) is *sp* hybridized.

10.89 For an octahedral AX_4Y_2 molecule only two different structures are possible: one with the two Y's next to each other like **(b)** and **(d)**, and one with the two Y's on opposite sides of the molecule like **(a)** and **(c)**. The different looking drawings simply depict the same molecule seen from a different angle or side.

It would help to develop your power of spatial visualization to make some simple models and convince yourself of the validity of these answers. How many different structures are possible for octahedral AX_5Y or AX_3Y_3 molecules? Would an octahedral AX_2Y_4 molecule have a different number of structures from AX_4Y_2? Ask your instructor if you aren't sure.

10.90 C has no *d* orbitals but Si does (3*d*). Thus, H_2O molecules can add to Si in hydrolysis (valence-shell expansion).

10.91 B_2 is $(\sigma_{1s})^2(\sigma^{\star}_{1s})^2(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\pi_{2p_y})^1(\pi_{2p_z})^1$. It is ***paramagnetic***.

10.92 The carbons are in sp^2 hybridization states. The nitrogens are in the sp^3 hybridization state, except for the ring nitrogen double-bonded to a carbon that is sp^2 hybridized. The oxygen atom is sp^2 hybridized.

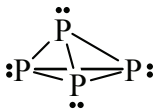
10.93 Referring to Table 10.5, we see that F_2^- has an extra electron in $\sigma^{\star}_{2p_x}$. Therefore, it only has a bond order of $\frac{1}{2}$ (compared with a bond order of one for F_2).

10.94 **(a)** Use a conventional oven. A microwave oven would not cook the meat from the outside toward the center (it penetrates).

(b) Polar molecules absorb microwaves and would interfere with the operation of radar.

(c) Too much water vapor (polar molecules) absorbed the microwaves, interfering with the operation of radar.

10.95

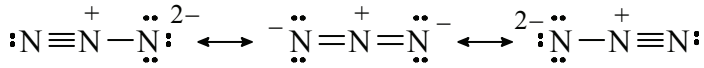


The four P atoms occupy the corners of a tetrahedron. Each phosphorus atom is sp^3 hybridized.

The P_2 molecule has a triple bond, which is composed of one sigma bond and two pi bonds. The pi bonds are formed by sideways overlap of 3*p* orbitals. Because the atomic radius of P is larger than that of N, the overlap is not as extensive as that in the N_2 molecule. Consequently, the P_2 molecule is much less stable than N_2 and also less stable than P_4, which contains only sigma bonds.

10.96 The smaller size of F compared to Cl results in a shorter F–F bond than a Cl–Cl bond. The closer proximity of the lone pairs of electrons on the F atoms results in greater electron-electron repulsions that weaken the bond.

10.97 Since nitrogen is a second row element, it cannot exceed an octet of electrons. Since there are no lone pairs on the central nitrogen, the molecule must be linear and *sp* hybrid orbitals must be used.



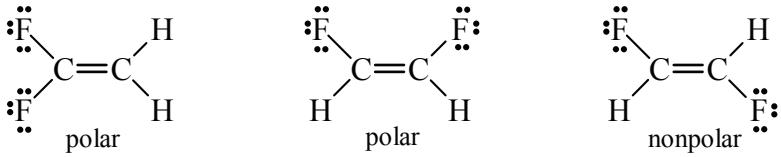
The $2p_y$ orbital on the central nitrogen atom overlaps with the $2p_y$ on the terminal nitrogen atoms, and the $2p_z$ orbital on the central nitrogen overlaps with the $2p_z$ orbitals on the terminal nitrogen atoms to form delocalized molecular orbitals.

10.98 1 D = 3.336×10^{-30} C·m

electronic charge (e) = 1.6022×10^{-19} C

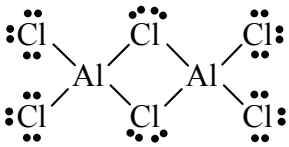
$$\frac{\mu}{ed} \times 100\% = \frac{1.92\ \text{D} \times \dfrac{3.336 \times 10^{-30}\ \text{C}\cdot\text{m}}{1\ \text{D}}}{(1.6022 \times 10^{-19}\ \text{C}) \times (91.7 \times 10^{-12}\ \text{m})} \times 100\% = \textbf{43.6\%}\ \text{ionic character}$$

10.99



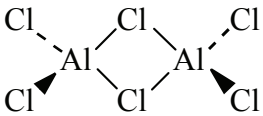
10.100 The second and third vibrational motions are responsible for CO_2 to behave as a greenhouse gas. CO_2 is a nonpolar molecule. The second and third vibrational motions, create a changing dipole moment. The first vibration, a symmetric stretch, does *not* create a dipole moment. Since CO, NO_2, and N_2O are all polar molecules, they will also act as greenhouse gases.

10.101 **(a)**



(b) The hybridization of Al in $AlCl_3$ is sp^2. The molecule is trigonal planar. The hybridization of Al in Al_2Cl_6 is sp^3.

(c) The geometry about each Al atom is tetrahedral.



(d) The molecules are nonpolar; they do not possess a dipole moment.

10.102 **(a)** A σ bond is formed by orbitals overlapping end-to-end. Rotation will not break this end-to-end overlap. A π bond is formed by the sideways overlapping of orbitals. The two 90° rotations (180° total) will break and then reform the pi bond, thereby converting *cis*-dichloroethylene to *trans*-dichloroethylene.

(b) The pi bond is weaker because of the lesser extent of sideways orbital overlap, compared to the end-to-end overlap in a sigma bond.

(c) The bond enthalpy is given in the unit, kJ/mol. To find the longest wavelength of light needed to bring about the conversion from *cis* to *trans*, we need the energy to break a pi bond in a single molecule. We convert from kJ/mol to J/molecule.

$$\frac{270\ \text{kJ}}{1\ \text{mol}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{molecules}} = 4.48 \times 10^{-22}\ \text{kJ/molecule} = 4.48 \times 10^{-19}\ \text{J/molecule}$$

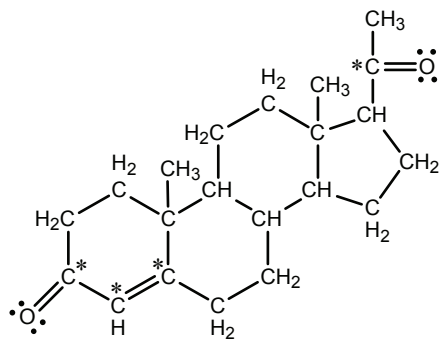
Now that we have the energy needed to cause the conversion from *cis* to *trans* in one molecule, we can calculate the wavelength from this energy.

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{4.48 \times 10^{-19}\ \text{J}}$$

$$\boldsymbol{\lambda = 4.44 \times 10^{-7}\ \text{m} = 444\ \text{nm}}$$

10.103 The complete structure of progesterone is shown below.

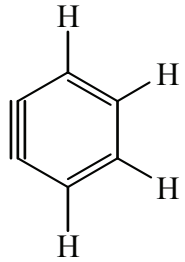


The four carbons marked with an asterisk are sp^2 hybridized. The remaining carbons are sp^3 hybridized.

10.104 In each case, we examine the molecular orbital that is occupied by the valence electrons of the molecule to see if it is a bonding or antibonding molecular orbital. If the electron is in a bonding molecular orbital, it is more stable than an electron in an atomic orbital (1*s* or 2*p* atomic orbital) and thus will have a higher ionization energy compared to the lone atom. On the other hand, if the electron is in an antibonding molecular orbital, it is less stable than an electron in an atomic orbital (1*s* or 2*p* atomic orbital) and thus will have a lower ionization energy compared to the lone atom. Refer to Table 10.5 of the text.

(a) H_2 **(b)** N_2 **(c)** O **(d)** F

10.105



The normal bond angle for a hexagon is 60°. However, the triple bond requires an angle of 180° (linear) and therefore there is a great deal of strain in the molecule. Consequently, the molecule is very reactive (breaking the bond to relieve the strain).

10.106 **(a)** Looking at the electronic configuration for N_2 shown in Table 10.5 of the text, we write the electronic configuration for P_2.

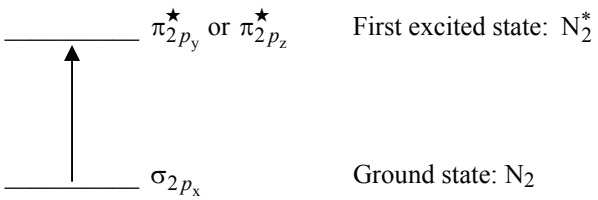
$$[\text{Ne}_2](\sigma_{3s})^2(\sigma_{3s}^{\star})^2(\pi_{3p_y})^2(\pi_{3p_z})^2(\sigma_{3p_x})^2$$

(b) Past the Ne_2 core configuration, there are 8 bonding electrons and 2 antibonding electrons. The bond order is:

$$\textbf{bond order} = \tfrac{1}{2}(8 - 2) = \mathbf{3}$$

(c) All the electrons in the electronic configuration are paired. P_2 is **diamagnetic**.

10.107 **(a)** From Table 10.5 of the text:



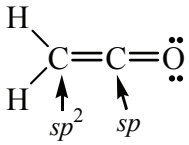
(b) The bond order for N_2 is 3. The bond order for N_2^* is $\tfrac{1}{2}(5 - 1) = 2$. N_2^* should have a longer bond length than N_2.

(c) N_2^* is diamagnetic. Electrons do not change their spins during transitions.

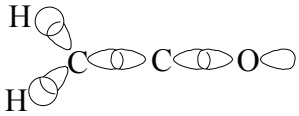
(d) $$\boldsymbol{E} = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{470 \times 10^{-9}\ \text{m}} = \mathbf{4.23 \times 10^{-19}\ J}$$

10.108 The Lewis structure shows 4 pairs of electrons on the two oxygen atoms. From Table 10.5 of the text, we see that these 8 valence electrons are placed in the σ_{2p_x}, π_{2p_y}, π_{2p_z}, $\pi^{\star}_{2p_y}$, and $\pi^{\star}_{2p_z}$ orbitals. For all the electrons to be paired, energy is needed to flip the spin in one of the antibonding molecular orbitals ($\pi^{\star}_{2p_y}$ or $\pi^{\star}_{2p_z}$). According to Hund's rule, this arrangement is less stable than the ground-state configuration shown in Table 10.5, and hence the Lewis structure shown actually corresponds to an excited state of the oxygen molecule.

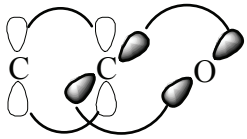
10.109



σ bonds



π bonds



10.110 **(a)** Although the O atoms are sp^3 hybridized, they are locked in a planar structure by the benzene rings. The molecule is symmetrical and therefore does not possess a dipole moment.

(b) 20 σ bonds and 6 π bonds.

10.111 Referring to Table 10.5 of the text, we see that C_2 and N_2 have a similar energy order for their molecular orbitals. Therefore, we expect CN^- to have the same order.

$$(\sigma_{1s})^2(\sigma_{1s}^\star)^2(\sigma_{2s})^2(\sigma_{2s}^\star)^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\sigma_{2p_x})^2$$

CO is isoelectronic with CN^- (both contain 14 electrons).

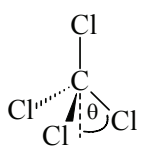
10.112 **(a)** $:\overset{-}{C}\equiv\overset{+}{O}:$

This is the only reasonable Lewis structure for CO. The electronegativity difference suggests that electron density should concentrate on the O atom, but assigning formal charges places a negative charge on the C atom. Therefore, we expect CO to have a small dipole moment.

(b) The Lewis structure shows a triple bond. The molecular orbital description gives a bond order of 3, just like N_2 (see Table 10.5 of the text).

(c) Normally, we would expect the more electronegative atom to bond with the metal ion. In this case, however, the small dipole moment suggests that the C atom may form a stronger bond with Fe^{2+} than O. More elaborate analysis of the orbitals involved shows that this is indeed the case.

10.113 CCl_4 can be represented by:



Let ρ be a C–Cl bond moment. Thus,

$$\rho = 3\rho\cos\theta$$

$$\cos\theta = \frac{1}{3} \qquad \theta = 70.5°$$

Tetrahedral angle = 180° – 70.5° = **109.5°**